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COMPLETE SPECIFICATION

Improvements in or relating to Resins

We, CHEMISCHE WERKE ALBERT, a German Body Corporate of Wiesbadan-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in or relating to copolymerisable mixtures of value in the production of neutron absorbing moulded bodies and surface coatings.

Several elements, such as boron, cadmium and certain lanthanide metals, are known to absorb low energy neutrons and are therefore suitable for use in protective coatings designed for staff exposed to such radiation. Suitable absorption media are in particular those which contain the above elements per se or as alloy components or in admixture with a neutron moderator. Known moderators are carbon, hydrogen, deuterium or oxygen and they may be used in their elementary form or in compounds e.g. as graphite, paraffin or heavy water.

Further, there have been proposed, as neutron moderators materials which comprise a synthetic resin, such as a polyester resin, an epoxy resin, or phenol aldehyde casting resin, or a butadiene polymer, as one component, and as the other component a mixture which contains a major proportion of compounds having a high ratio of hydrogen atoms to all other atoms, and a minor proportion of boron or boron-compounds. Suitable boron compounds in this previously proposed material are for example boric acid, boron oxide, boron carbide, borax or boric acid esters, such as glyceryl borate. Suitable compounds in which the ratio of hydrogen atoms to all other atoms is high, include polyethylene, butyl rubber, paraffin wax, polyisobutylene, and polyisoprene. Copolymerisation products of unsaturated polyester resins and vinyl phenyl boric acids or esters thereof have also been proposed, as neutron moderators in the form of moulded bodies or coatings.

According to the present invention there is provided a copolymerisable mixture free from elements having an atomic number greater than 9 (other than neutron moderators) and from lithium, of a polyester having polymerisable olefinic bonds, which polyester is derived from a polycarboxylic acid, preferably an α,β-ethylenically unsaturated acid and a polyhydric alcohol, or derived from an adduct of a diester of a dicarboxylic acid with a monoallylacetal of an at least trihydric alcohol, or an adduct of an ester of a dicarboxylic acid and a polyhydric alcohol with an unsaturated diacetal, and an ethylenically unsaturated monomer said mixture containing at least 0.3% by weight of boron as a neutron moderator, wherein, either the acid component of said polyester is derived in part from boric acid, or the ethylenically unsaturated monomer is at least in part an ester of boric acid and an unsaturated alcohol or wherein either said polyester or the ethylenically unsaturated monomer or both contain boron hydride or boron chloride.

The amount of boron to be present in the composition depends on the strength of the radiation and the thickness of the sheet etc. prepared from the composition, generally however, it should be at least 0,3% by weight and not more than 10% by weight. A range of from 0.3 to 5% by weight has been found generally convenient.

Preferably fluorine is also absent from the

[Price 4s. 6d.]

composition according to the invention i.e. elements having an atomic number greater than 8 and lithium should be absent.

Compositions containing elements with an atomic number greater than 9 or preferably 8 with the exception of cadmium and lanthanides which have the property of absorbing neutrons are unsuitable for use in the composition according to the invention, since on irradiation with neutrons they can emit secondary β- and γ-rays.

The compositions according to the invention can be used in the production of moulded bodies and coatings.

Also according to the invention there is provided a process for the production of said copolymerisable mixtures comprising forming a polyester resin, which is free from elements having an atomic number greater than 9 and from lithium, from a polyhydric alcohol, a polyfunctional carboxylic acid or from a reaction product thereof with a diacetal containing two olefinic bonds. The diacetal is an optional constituent in this process.

The polyester resins can thus be obtained for example by chemically building boron into conventional polyester resins in the form of a compound such as boric acid, or into polyester resins which besides ester bonds also contain ether bonds and are obtained for example by the addition of esters of dicarboxylic acids and polyhydric alcohols, which contain hydroxyl groups, to unsaturated diacetals such as diallylidene pentaerythritol which final products therefore, are also called polyetheracetals, or by addition of diesters of a dicarboxylic acid, which contain no aliphatic treble bond together with a monoallyl acetal of an at least trihydric alcohol which still contains a reactive hydroxyl group.

This introduction of boric acid or a compound which is a functional equivalent of boric acid, such as esters of boric acid, can be achieved for example by carrying out the esterification of the polyhydric alcohols and the polyfunctional acids in the presence of boric acid or its aliphatic or aromatic esters such as triethyl, triamyl, triallyl, or triphenyl borate. The modification of the normal procedures for the production of polyesters is generally not necessary. For example it is possible also to work at elevated pressure. In the place of the above mentioned boron compounds, a boron hydride or boron chloride may be used but are not preferred.

Since boron-free polyester resins contain olefinically unsaturated groups which are copolymerisable with ethylenically unsaturated monomers, such as styrene, the boron can also be incorporated into the resin in the form of unsaturated esters, such as for example allyl or vinyl borates.

During the preparation of the copolymerisation products from unsaturated polyester resins and ethylenically unsaturated monomers, no heavy metal accelerators such as for example cobalt naphthenate or cobalt octoate may be used since, as a rule, such heavy metals form on bombardment with neutrons, isotopes, such as Co^{60}, which emit harmful secondary radiation. If therefore accelerators are necessary the conventional tertiary amine accelerators are preferred. In general care should be taken that no components are introduced into the polyesters, which contain elements with an atomic number greater than 9. For instance hydrogen chloride gas produced for example when boron trichloride is used instead of boric acid, should be removed completely from the reaction product.

The resins prepared according to the invention are light to colourless and have a slightly lower viscosity than comparable boron-free products. They are suitable both for radiation-protecting coatings and for neutron moderating moulded bodies of any type, e.g. for container material or for insulating purposes for deflecting radioactive rays, e.g. in the form of insulating plates.

The shaped bodies and coatings according to the present invention exert a marked absorbing action on neutrons. If, for example, a plate 10 cm thick of the boron-containing polyester of the example is irradiated with a neutron source of 200mC, the neutrons having an energy of about 12Mev, no neutrons penetrate through the plates. The neutrons are thus completely absorbed (thermalised) and no dispersion or reflection occurs. Any secondary α-radiation resulting is not dangerous since it will be of narrow range.

The usual fillers, namely those which consist of elements with an atomic number below 9 and, as a rule, are also free of lithium, may be added to the boron containing polyester resins prepared according to the invention.

The protection against neutrons may be increased by adding other additional neutron absorbing substances such as for example elementary boron, boron carbide, boron oxide, or boron nitride. Again it will be noticed that all these compounds are compounds of boron which elements having a low atomic number, i.e. below 9. However, other substances also having a neutron absorbing action such as cadmium, or one or more of the lanthanides such as europium, gadolinium or samarium in elementary form or in the form of their compounds preferably compounds with elements of low atomic numbers can be used. Examples of such compounds are cadmium borate, cadmium carbonate, cadmium oxide or the corresponding lanthanide compounds. In principle the alloys of said metals may also be used but care must be taken in the choice of the alloy components to ensure that no heavy metals are introduced which form radiation producing products on neutron bombardment. The amount of additional ray-absorbing filler depends upon the intensity of the

radiation to be shielded off. Good results may be obtained with 0.1% by weight of the resin, the radiation protection effect being dependent also upon the thickness of the layer. The upper limit of filler depends on the binding power of the synthetic material or resins. Generally they are used in an amount of about 0.5 to about 20% calculated on the weight of the resin. If desired there may be added other fillers which will not produce any secondary radiation, e.g. carbon.

Masses having a supporting web which consists of elements preferably possessing an atomic number up to 8, e.g. cotton, a polyamide, polyacrylonitrile, or polyester fabrics are also suitable. Glass fibres are also usable if suitable safety measures are taken against the possibility of secondary radiation occurring. Fluorine-containing support webs may also be used. The fabric may also be present in an amount of 0.5 to 20% calculated on the weight of the resin.

The properties of the final products are also dependent on the ratio and the nature of the other reactants used and also on the degree of esterification. Generally the reaction is carried out until the polyester resin has an acid value of not more than 70, preferably until the resin has an acid value between 20 and 60. However, the resin may also have a still lower acid value, e.g. as low as 5. The polyether acetals generally have however, lower acid values, mostly below 40, and hydroxy values below 100.

If the polyester resins are to be used in admixture with solvents, the esterification may be carried out in the presence of suitable solvents or diluents, for example high boiling aliphatic or aromatic or terpene hydrocarbons. In the case of terpenes reaction between the solvent and product may occur if unsaturated dicarboxylic acids or functional derivatives thereof are used in the preparation of the polyester. Solvents or diluents may, however, also be used in the esterification when the resins are not intended to be used in admixture with solvents.

The polyester resins may also be modified by adding a minor amount of resinic acids or long-chain fatty acids having, for example, from 12 to 22 carbon atoms. These acids may be used in an amount of up to 50 equivalent per cent, calculated on the dicarboxylic acid or derivative thereof and in general in an amount of 1 to 20 equivalent per cent, again calculated on the dicarboxylic acid.

Preferred dicarboxylic acids for use in the process according to the invention are α,β olefinically unsaturated dicarboxylic acids, for example maleic acid, fumaric acid, itaconic acid, citraconic acid, and mesaconic acid. Other suitable dicarboxylic acids are those containing no polymerisable aliphatic bonds, for example, succinic and glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic or terephthalic acid or the hexahydrogenation products of these acids or endomethylene tetra- or hexahydrophthalic acid.

The last-mentioned carboxylic acids are suitably applied in an amount of up to 50 equivalent % only. The anhydrides where they exist of the dicarboxylic acids may also be used in place of the acids themselves.

Polyhydric alcohols which may be used for the manufacture of the polyester resins or of the polyether acetals are for example ethylene glycol; diethylene glycol; triethyleneglycol; 1,2-propyleneglycol; 1,3-propanediol; a butanediol, pentanediol or hexanediol such as 1,3-butanediol; 2,2 - dimethylpropane - 1,3 - diol; 1,4-dimethylolcyclohexane; Δ-2,3-butene-1,4-diol; a hydrogenated bisphenol (i.e. hydrogenated *p,p'*-dihydroxydiphenylpropane - 2,2 or homologues thereof); partially etherified or acetalized products of alcohols containing at least three hydroxy groups, which are preferably etherified or acetalized to such an extent that they still contain two free hydroxy groups, e.g. partially etherified or acetalized glycerol, trimethylolethane, trimethylolpropane, hexanetriol or pentaerythritol. The acetal or ether radicals may be saturated or olefinically unsaturated radicals in which the ethereal or acetal oxygen is bound to an aliphatic carbon atom and which contain up to 10, preferably 3 to 7, carbon atoms. Suitable radicals are e.g. the methyl, ethyl, propyl, isopropyl, allyl, butyl or benzyl radicals or the corresponding acetal groups. Other suitable polyhydric alcohols are the various dimethylolbenzenes, dimethylol toluenes and dimethylol xylenes; addition products of alkylene oxides such as ethylene oxide, propylene oxide and butylene oxide with dihydric alcohols, e.g. those described above, or with dihydric phenols, such as resorcinol, hydroquinone, 4,4'-dihydroxydiphenylmethane, -ethane, -propane or homologues thereof.

If desired, higher polyhydric alcohols may be used in addition to the dihydric alcohols, examples of such alcohols being glycerol, trimethylolethane, trimethylolpropane and hexanetriol. Preferably, however, these alcohols are used to such an extent, that the portion of the "excess" hydroxy groups (i.e. the number of the free hydroxy groups per alcohol molecule greater than two) is not higher than 10 equivalent per cent and preferably not higher than 7 equivalent per cent of the hydroxy groups contained in the mixture. Such alcohols may also be used together with monohydric alcohols or monocarboxylic acids in amounts about equivalent to the excess hydroxy groups.

In addition to the dicarboxylic acids mentioned above, there may also be used other bifunctional acids such as monohydroxy monocarboxylic acids, in which the hydroxy groups may be esterified at the temperatures em-

ployed, e.g. in a molar ratio of dicarboxylic acid to monohydroxy monocarboxylic acid of between 5:1 and 1:2. Suitable acids are for example ricinoleic acid and 12-hydroxystearic acid. The bifunctional acids may also be used together with higher polycarboxylic acids, such as pyromellitic acid. However, these polycarboxylic acids are preferably employed in an amount such that the "excess" carboxylic groups (i.e. the number of carboxylic groups per molecule of acid greater than two) are present in an amount not higher than 10 equivalent per cent, preferably not higher than 7 equivalent per cent of the carboxylic groups contained in the mixture. Such polybasic carboxylic acids may also be used together with monocarboxylic acids, preferably benzoic acid or fatty acids having at least 12 carbon atoms, or with monohydric alcohols, in amounts substantially equivalent to the "excess" carboxylic groups.

As polyester resins there may for example also be used products which have been obtained by esterifying polybasic carboxylic acids preferably dicarboxylic acids or anhydrides thereof, with polyhydric alcohols and dicyclopentadiene preferably in two stages. In the latter case the reactants are suitably reacted in the first stage at a temperature below the boiling temperature of the dicyclopentadiene (generally below 140° C) and then in the second stage at a temperature above 160° C.

The resins containing olefinical unsaturation either derived from unsaturated dicarboxylic acids or from the alcohol component, e.g. Δ-2,3-butene-1,4-diol or from both are copolymerized e.g. at a temperature in the range from 0 to 150° C, with ethylenically unsaturated polymerisable monomers which are free from lithium and elements having an atomic number above 9 to yield synthetic resins or polymerisation products of good mechanical properties.

According to a further feature of the invention, therefore, there is provided a process for the preparation of synthetic resins which comprises copolymerising an unsaturated polyester or polyacetal resin produced by the process of the invention with an ethylenically unsaturated polymerisable monomer preferably in the presence of a polymerisation catalyst.

Suitable ethylenically unsaturated polymerisable monomers include, for example, meta- and para-vinyl toluene, N-vinyl pyrrolidone, styrene, α-methylstyrene, vinyl acetate, vinyl propionate, allylacetate, allylpropionate, diallyl maleate, diallyl fumarate, dially adipate, diallyl azelate, diallyl sebacate, diallyl phthalate, triallylcyanurate; methyl-, ethyl-, propyl-, (primary, secondary, tertiary or iso) butyl-, amyl-, hexyl-, octyl- or allylacrylate or methacrylate, diallylitaconate, vinyl or allyl borate or a mixture of such monomers. Preferred monomers are those compounds in which the group $—CH=CH_2$ is bound to a negative radical such as a benzene nucleus or an ester group. Other preferred monomers are those which contain no conjugated double bonds and are liquid under ordinary conditions. The amount of olefinically unsaturated monomer may vary between wide limits depending on the desired application. Thus it may be between 30 and 50% of the weight of the polyester resin, but it may be used in a far larger, e.g. 80%, or smaller amount, e.g. 10%.

Suitable polymerisation catalysts are organic peroxide catalysts, e.g. benzoylperoxide, acetylperoxide, tert.-butylperoxide or -hydroperoxide, lauroyl peroxide, cyclohexanone peroxide, methyl-ethylketone peroxide, methylisobutylketone peroxide, dibenzaldiperoxide, tert.-butylper - benzoate, ditert. - butyl - diperphthalate, or azoisobutyronitrile. If desired the polymerisation may be promoted by accelerators such as tertiary amines, e.g. dimethylaniline, dimethyl-p-toluidine, diethylethanolamine, triethylamine, or tributylamine.

Of course in all cases mixtures of several compounds may be used instead of single compounds, i.e. there may be applied several carboxylic acids, alcohols, esters, monomers etc.

In order that the invention may be well understood the following example is given by way of illustration only:—

EXAMPLE

A polyester having an acid value of 61 is produced by a conventional method from 1.2 mols of 1,2-propanediol, 0.5 mol of phthalic anhydride, 0.25 mol of maleic anhydride and 0.25 mol of boric acid, a solution of which in the same amount of ethyleneglycolmonoethyl ether at 20° C has a viscosity of about 40 cp. After it has been dissolved in styrene to yield a solution of 75% solids content, the resin is activated with 0.5% of a benzoyl peroxide paste. The mixture is either cast into a mould or pressed in a mould and therein hardened at an elevated temperature. A hard shaped body is obtained, which if exposed to high energy neutrons, absorbs them.

WHAT WE CLAIM IS:—

1. A copolymerisable mixture free from elements having an atomic number greater than 9 (other than neutron moderators) and from lithium, of a polyester having polymerisable olefinic bonds, which polyester is derived from a polycarboxylic acid and a polyhydric alcohol, or derived from an adduct of a diester of a dicarboxylic acid with a monoallylacetal of an at least trihydric alcohol, or an adduct of an ester of a dicarboxylic acid and a polyhydric alcohol with an unsaturated diacetal, and an ethylenically unsaturated monomer said mixture containing at least 0.3% by weight of boron as a neutron moderator, wherein, either

the acid component of said polyester is derived in part from boric acid, or the ethylenically unsaturated monomer is at least in part an ester of boric acid and an unsaturated alcohol or wherein either said polyester or the ethylenically unsaturated monomer or both contain boron hydride or boron chloride.

2. A copolymerisable mixture as claimed in claim 1 having a boron content of not more than 10% by weight.

3. A copolymerisable mixture as claimed in claim 1 or 2, wherein the boron content is in the range of from 0.3 to 5% by weight.

4. A copolymerisable mixture as claimed in any of claims 1 to 3, containing no element having an atomic number greater than 8.

5. A copolymerisable mixture as claimed in any of claims 1 to 4 wherein the acid component of the polyester is an α,β-unsaturated dicarboxylic acid.

6. A composition comprising a copolymerisable mixture as claimed in any of claims 1 to 5 containing an additional neutron absorbing substance.

7. A composition as claimed in claim 6 wherein the additional neutron absorbing substance is boron or a compound of boron with an element the atomic number of which is not higher than 8.

8. A composition as claimed in claim 6 wherein the additional neutron absorbing substance is cadmium, europium, gadolinium, samarium or a mixture thereof or a compound of such materials which is free from other elements having an atomic number above 9.

9. A plastic or synthetic resin composition comprising a boron containing copolymerisable polyester resin mixture or polyester resin composition as claimed in any of the preceding claims.

10. A composition as claimed in claim 9 containing a carrier fabric free from elements of an atomic number greater than 9.

11. A composition as claimed in claim 10 wherein the carrier fabric is present in an amount of 0.5 to 20%, calculated on the weight of the resin.

12. A composition as claimed in claim 1 substantially as herein described.

13. A composition as claimed in claim 6 substantially as herein described.

14. A shaped body or coating comprising a polyester resin or polyester resin composition as claimed in any of the preceding claims.

15. A process for the production of a composition or mixture as claimed in any of claims 1 to 13 comprising forming a polyester resin which is free from elements having an atomic number greater than 9 and from lithium, from a boron compound, a polyhydric alcohol and a polyfunctional carboxylic acid and a diacetal containing two olefinic bonds.

16. A process as claimed in claim 15 wherein the boric acid content is derived from a compound which is a functional equivalent of boric acid.

17. A process as claimed in claim 15 or claim 16 wherein the polyester resin is a polyether acetal and has an acid value below 40 and a hydroxy value below 100.

18. A process for the production of a composition or mixture as claimed in any of claims 1 to 13 comprising forming a polyester resin which is free from elements having an atomic number greater than 9 and from lithium, from a boron compound, a polyhydric alcohol and a polyfunctional carboxylic acid.

19. A process as claimed in claim 18 wherein the polyester resin has an acid value of not more than 70.

20. A process as claimed in claim 19, wherein the acid value is from 20 to 60.

21. A process as claimed in any of claims 18 to 20 in which the esterification is carried out in the presence of a solvent or diluent.

22. A process as claimed in any of claims 18 to 21 in which the polyester resin is modified with a resinic or long chain fatty acid having from 12 to 22 carbon atoms in an amount of up to 50 equivalent per cent based on the dicarboxylic acid or derivative thereof.

23. A process as claimed in claim 22 in which said resinic or long chain fatty acid is employed in an amount of from 1 to 20 equivalent per cent based on the dicarboxylic acid or derivative thereof.

24. A process as claimed in any of claims 15 to 23 in which said polyfunctional carboxylic acid is an α,β-olefinically unsaturated dicarboxylic acid.

25. A process as claimed in claim 24 in which said dicarboxylic acid is maleic acid, fumaric acid, itaconic acid, citraconic acid or mesaconic acid.

26. A process as claimed in any of claims 13 to 25 in which said polyhydric alcohol is a dihydric alcohol.

27. A process as claimed in claim 26 in which said dihydric alcohol is ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,3-propanediol, 1,3-butanediol, 2,2-dimethylpropane-1,3-diol, 2-ethyl-2-butyl-propane-1,3-diol, 1,4-dimethylolcyclohexane, Δ-2,3-butene-1,4-diol, or hydrogenated *p,p*, - dihydroxy - diphenylpropane - 2,2- or a homologue thereof.

28. A process as claimed in any of claims 15 to 27 in which said polyhydric alcohol is a partially etherified or acetalised polyhydric alcohol containing two free hydroxy groups.

29. A process as claimed in claim 28 in which the acetal or ether oxygen atom is bound to an aliphatic carbon atom of a radical containing up to 10 carbon atoms.

30. A process as claimed in any of claims 26 to 29 in which there is also employed a tri- or higher hydric alcohol in such an amount

that the amount of excess hydroxy groups as herein defined is not higher than 10 equivalent per cent.

31. A process as claimed in claim 30 in which the amount of said hydroxy groups is not higher than 7 equivalent per cent.

32. A process as claimed in claim 30 or claim 31 in which a monohydric alcohol or monocarboxylic acid is employed in an amount equivalent to the excess hydroxy groups.

33. A process as claimed in any of claims 15 to 32 in which there is also employed a monohydroxy monocarboxylic acid in a molar ratio of monohydroxy monocarbxylic acid to dicarboxylic acid of from 2:1 to 1:5.

34. A process as claimed in claim 33 in which said monohydroxy monocarboxylic acid is recinoleic acid and/or 12-hydroxy stearic acid.

35. A process as claimed in any of claims 15 to 34 in which there is also employed a higher polycarboxylic acid in an amount such that the amount of excess carboxylic groups as herein defined is not greater than 10 equivalent per cent.

36. A process as claimed in claim 35 in which the amount of excess carboxylic groups is not higher than 7 equivalent per cent.

37. A process as claimed in claim 35 or claim 36 in which there is also employed a monocarboxylic acid or a monohydric alcohol in an amount equivalent to the excess carboxylic groups.

38. A process as claimed in claim 37 in which said monocarboxylic acid is benzoic acid or a fatty acid containing at least 12 carbon atoms.

39. A process as claimed in any one of claims 18 to 38 wherein the polyester resin is obtained by esterifying polybasic carboxylic acids or anhydrides thereof with polyhydric alcohols and dicyclopentadiene in two stages, the first stage being reacted at a temperature below the boiling point of dicyclopentadiene and the second stage at a temperature above 160° C.

40. A process as claimed in claim 39 wherein the temperature of the first stage is below 140° C.

41. A process as claimed in claim 15 substantially as herein described.

42. Polyester or polyetheracetal resins when prepared by a process as claimed in any of claims 15 to 41.

43. Polyester or polyetheracetal resins as claimed in claim 42 when derived from an α,β-olefinically unsaturated dicarboxylic acid or derivative thereof.

44. A solution of a polyester or polyetheracetal resin as claimed in claim 43 in an ethylenically unsaturated polymerisable monomer free from elements having an atomic number above 9 and from lithium.

45. A solution of a polyester or polyether acetal resin as claimed in claim 43, free from elements having an atomic number above 9 and from lithium, which polyester or polyether acetal may be free from boron in an ethylenically unsaturated polymerisable monomer consisting of or comprising a boron-containing compound.

46. A process for the preparation of synthetic resins which comprises copolymerising an unsaturated polyester or polyetheracetal resin as claimed in claim 43 with an ethylenically unsaturated polymerisable monomer free from elements having an atomic number above 9 and from lithium.

47. A process as claimed in claim 46 which comprises copolymerising a solution as claimed in claim 44 or in claim 45.

48. A process as claimed in claim 46 or claim 47 in which the polymerisable monomer contains no conjugated double bonds and is liquid under normal conditions.

49. A process as claimed in any of claims 46 to 48 in which the ethylenically unsaturated monomer is employed in an amount of from 10 to 80% by weight based on the weight of unsaturated polyester resin.

50. A process as claimed in claim 49 in which the ethylenically unsaturated monomer is employed in an amount of from 30 to 50% by weight based on the weight of unsaturated polyester resin.

51. A process as claimed in any of claims 46 to 50 in which the polymerisation is carried out in the presence of a polymerisation catalyst.

52. A process as claimed in any of claims 46 to 51 in which the polymerisation is carried out in the presence of an accelerator.

53. A process as claimed in claim 46 substantially as herein described.

54. Synthetic resins when obtained by a process as claimed in any of claims 46 to 53.

55. Coatings and shaped bodies optionally reinforced, comprising a synthetic resin as claimed in claim 54.

56. A copolymerisable mixture which is free from elements having an atomic number greater than 9 and from lithium of an α,β-ethylenically unsaturated polyester, derived from a polycarboxylic acid and a polyhydric alcohol, or derived from an adduct of a diester of a dicarboxylic acid with a monoallylacetal of an at least trihydric alcohol or an adduct of an ester of a dicarboxylic acid and a polyhydric alcohol with an unsaturated diacetal, derived from a poly- and polyester containing at least 0.1% by weight of boron as a neutron

moderator, wherein the acid component of said polyester is derived at least in part from boric acid.

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